Pulsed-laser annealing of implanted layers in GaAs

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Semi-insulating Si-implanted GaAs has been irradiated by a ruby-laser pulse ($\lambda = 0.694$ μm, $t_p = 15$ ns) without using an encapsulant. Hall-effect measurements indicate that the values of sheet resistance, effective sheet electron concentration, and effective electron mobilities are roughly comparable to those of conventionally annealed samples. TEM micrographs show a difference in the defect structure after these two types of annealing.

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Thermal annealing of implanted layers in GaAs typically requires the use of an encapsulant (e.g., SiO_2,Si_3N_4, AlN, AlO_xN_{1-x}, etc.).[1,2] The encapsulant is necessary for the prevention of the dissociation of As at the relatively high annealing temperatures ($\geqslant$800 °C) needed for good activation of the implanted ions. Although considerable effort has been made over the last few years in search of the right kind of an encapsulant for annealing,[1,2] no encapsulant is found to be perfect. The preservation of the stoichiometry of GaAs in the implanted region after annealing is always in question due to the escape of As and/or the out-diffusion of Ga through the encapsulant. As a consequence, the electrical properties of the implanted layer are often found to be irreproducible, depending on the encapsulant used and the method of depositing it. This problem with encapsulants makes it difficult to obtain the reproducibility of implantation doping which is a potential advantage of ion implantation. Therefore, the possibility of annealing implanted layers in GaAs by a laser pulse, without using an encapsulant, seems attractive.

The use of high-power laser pulses to anneal implanted layers in Si [3-8] and GaAs[4,6,9-11] has been reported. In this paper we report on the annealing of Si^+-implanted GaAs by a ruby-laser pulse without using an encapsulant. The properties of the pulsed-laser-annealed implanted layers are compared with those obtained after thermal annealing.

Semi-insulating ⟨100⟩ wafers of Cr-doped GaAs were implanted at room temperature with 300-keV Si ions to a dose of about 10^{15} cm^{-2}. In order to minimize channeling, the ion beam was oriented at an angle of about 10° to the normal to the wafer surface. Laser annealing was accomplished in air by a Q-switched ruby-laser ($\lambda = 0.694\,\mu$m) pulse of about 15-ns duration and with a spot diameter of about 1 cm. The incident energy densities employed were 1.0 or 1.2 J/cm^2. For comparison purposes, similar implanted wafers were annealed thermally at 800, 850, or 900 °C in H_2 atmosphere after encapsulation with a Si_3N_4 film about 2000 Å thick.

A comparative summary of the results of Hall-effect measurements made on some of the laser-annealed and ther-

TABLE I. Comparison of the sheet resistance ρ_s, the ratio of the effective sheet electron concentration $N_{s,e}$ to the implantation dose N_d, and the effective mobility μ_e for semi-insulating GaAs implanted with Si and annealed thermally under an encapsulant or by a ruby lasr pulse.

	Si→GaAs, 300 keV, RT, 1×10^{15} cm^{-2}				
		Thermal anneal Si_3N_4 encapsulant		Ruby-laser anneal $t_p = 15$ ns No encapsulant	
	800 °C-30 min – H_2	850 °C-30 min – H_2	900 °C-30 min – H_2	1.0 J/cm^2	1.2 J/cm^2
ρ_s (Ω/□)	247	111	23	447	120
$N_{s,e}/N_d$	5.9×10^{-1}	1.9×10^{-2}	1.4×10^{-1}	5.0×10^{-2}	1.4×10^{-1}
μ_e (cm^2/V s)	2.4×10^3	1.7×10^3	1.2×10^3	2.8×10^2	3.7×10^2

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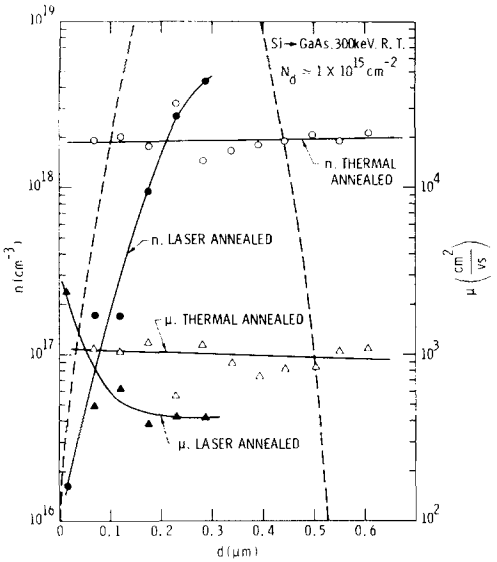

FIG. 1. Depth profiles of the electron concentration n and of the electron mobility μ measured on a sample irradiated with a 1.2-J/cm^2 ruby-laser pulse. The dashed line is the calculated LSS profile using Gaussian approximation (Ref. 13). Corresponding profiles for a thermally annealed sample (900 °C-30 min – H_2) are also given.

mally annealed samples is given in Table I, where the values of sheet resistance ρ_s, the ratio of the effective sheet electron concentration to the implantation dose ($N_{s,e}/N_d$), and the effective electron mobility μ_e are tabulated. The measurements were made after etching Van der Pauw–type mesas provided with Au-Ge/Pt Ohmic contacts.[12] The data in Table I show comparable values of ρ_s and $N_{s,e}/N_d$ for both the samples annealed by the laser pulses without an encapsulation and the samples annealed thermally using a Si_3N_4 encapsulant. The relatively low values of μ_e for the laser-annealed samples may be due to the residual ion damage remaining after laser irradiation in certain small regions of the wafers due to the nonuniformity of the beam spot. Profiles of the electron concentration n and the electron mobility μ obtained by successive stripping of surface layers combined with Hall-effect and resisivity measurements[12] are given in Fig. 1. Loss of an Ohmic contact prevented the extension of the profiles for the laser-annealed sample beyond the depth shown. However, the maximum electron concentration of the laser-annealed sample is seen to exceed that of the thermally annealed sample by at least a factor of 2. Whether the position of the maximum in this distribution agrees with the position of the calculated LSS distribution[13] (dashed line) cannot be deduced from the result. On the other hand, it is interesting to note that the electron concentration profile for the laser-annealed sample agrees better with the LSS distribution near the surface, as compared to the profile for the thermally annealed sample. The mobility for the laser-annealed sample appears to be less than that of the thermally annealed sample almost everywhere.

Good single-crystal quality of the implanted layers after laser irradiation was demonstrated by transmission electron microscopy measurements. Figure 2 shows TEM micrographs obtained from (a) the laser-annealed (1 J/cm^2) and (b) the thermally annealed (850 °C-30 min – H_2) samples (see Table I). Both samples are found to be good single crystals, as indicated by the diffraction picture with the sharp Kikuchi pattern shown in the inset of Fig. 2(a). The occurrence of randomly scattered faint spots in the picture obtained for the laser-annealed sample [Fig. 2(a)] probably indicates the existence of unidentified imperfections located in the first few hundred Angstroms of the implanted and annealed layer. The micrograph for the thermally annealed sample [Fig. 2(b)] shows a high density of disclocation loops, not found in the laser-annealed sample.

In conclusion, it appears that implanted layers in GaAs can be annealed by a laser pulse without using an encapsulant. From the technological point of view, considerable attention is needed in optimizing the laser-beam parameters for obtaining uniform implanted layers over large areas.

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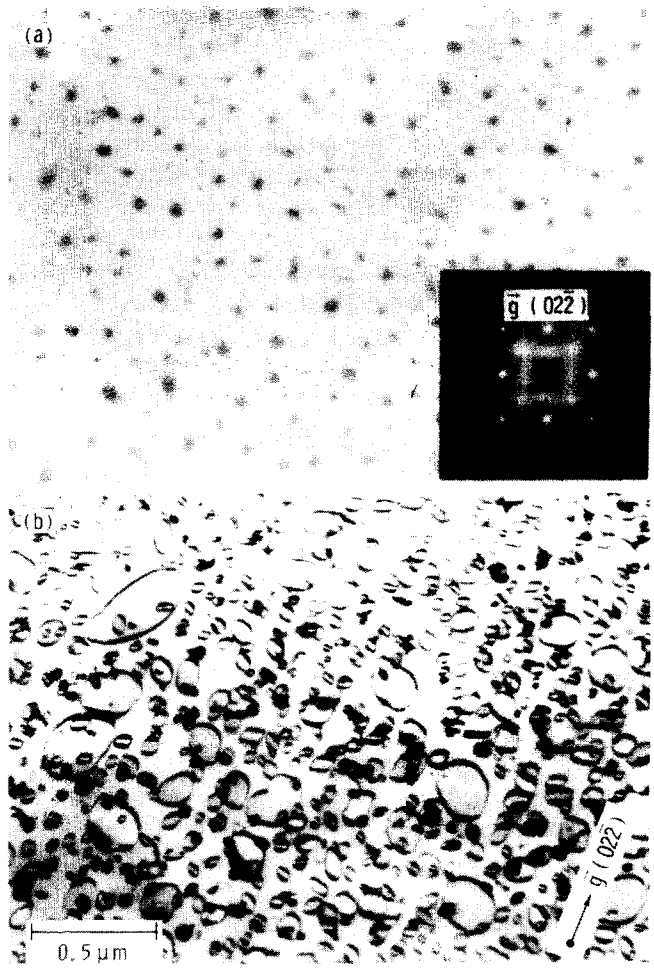

FIG. 2. TEM micrographs obtained from (a) the laser-annealed (1 J/cm^2) and (b) the thermal annealed (850 °C-30 min – H_2) samples. The diffraction pattern in the inset shows good single-crystal quality for both cases.

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Chemical origin of the space-charge layer in cuprous oxide front-wall solar cells[a)]

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Using Auger electron spectroscopy, the region near the front contact of cuprous oxide front-wall solar cells was investigated. In cells showing large photovoltages, a maximum of the copper concentration being by about 4 at.% higher than the bulk concentration was observed at a distance of 70 Å from the metal-semiconductor interface. If the photovoltage was low a copper maximum adjacent to the interfacial layer was found, instead. It is concluded that changes of the stoichiometry of cuprous oxide must be taken into account in order to explain the origin of the space-charge layer in Cu_2O front-wall cell.

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Cuprous oxide is an attractive starting material for solar cells for low-cost terrestrial conversion of solar energy to electricity.[1-4] When compared with more-developed types of solar cells the performance of Cu_2O solar cells is still poor, however. The best cells, which are all front-wall cells, have efficiencies of about 1%. Calculations show this value is expected to increase by a factor of 10 if some critical parameters can be improved.[1,3]

Besides the bulk properties of Cu_2O solar cells, the properties of the space-charge layer require additional investigations. In this work, the chemical composition near the front contact of Cu_2O front-wall cells is investigated using Auger electron spectroscopy (AES) in combination with Ar-ion sputtering.

Cuprous oxide layers were prepared according to the method used previously for the fabrication of back-wall cells,[5] i.e., by thermal oxidation of a copper sheet (purity 99.9%, thickness 0.5 mm) at 1050 °C for 1 min in air at atmospheric pressure. The oxidation was stopped by quenching in water. This procedure gives red layers of Cu_2O with thicknesses of about 20 μm and very good adherence to their copper substrates. Their structure is columnar, i.e., the grain boundaries are perpendicular to the copper substrate, and the mean grain diameter corresponds approximately to the thickness of the layer.

The Cu_2O layers were etched in nitric acid (60%) saturated with sodium chloride and in a solution of ammonium persulphate in water, rinsed in flowing water and dried between sheets of filter paper.

If a semitransparent gold or copper contact was deposited on a layer prepared by this method, an open-circuit photovoltage of about 10 mV under 100-mW cm^{-2} radiation from a tungsten halogen lamp with a 2-mm Schott KG2 filter was measured. However, a photovoltage of about 300 mV and an efficiency near 1% (taking into account the transmission of the metal contact) was obtained if chemical etching was followed by ion etching. The latter treatment was performed in a simple dc sputtering system, using air as the sputtering gas. Ion etching belongs to the class of treatments which have been known to lead to blocking layers in Cu_2O solar cells.[6] It has been chosen here because of its simplicity and its good reproducibility.

The parameters of the dc glow discharge were as follows: 800-V applied voltage, 20-mA discharge current, 20 Pa air pressure, and 5-min duration of the treatment. During

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